# Removal of clay and blue-green algae particles through zeta potential and particle size distribution in the dissolved air flotation process

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**Abstract** The raw water characteristics of a water treatment plant in Korea are mainly dependent on two major factors: the clay particles attributed to rainfall and blue-green algae in reservoirs. In this work, zeta potential and particle size distributions of clay and algae particles, which are the important parameters affecting their removal efficiency, were measured to investigate the behavior and removal characteristics of particles under various conditions. The results showed that the zeta potential of blue-green algae was more sensitive to treatment conditions than clay, and it fluctuated highly with coagulant dosage, suggesting that the control of zeta potential is important for effective removal of algae particles. On the other hand, the range of particle size distribution that remained from the preliminary sedimentation tank was generally smaller than for flotation. However, the zeta potential of the remaining particles was either close to the isoelectric point or positive, and the particles were not so hard to remove for that reason. In the final analysis, for simultaneous removal of clay and algae particles, a sufficient zeta potential difference must be formed not only for algae particles but also for small clay particles from the sedimentation tank in the dissolved air flotation process.

**Keywords** Algae; clay; collision efficiency; dissolved air flotation; particle size distribution; zeta potential

## Introduction

Many reservoirs have been constructed in Korea to store water resources because stream and river waters flow out rapidly because of the geomorphologic steep slope of the land. The source waters in reservoirs generally contain lower density algal particles because of eutrophication. The solids are hardly removed in the sedimentation unit because of their tendency to float. Actually, many conventional water treatment plants in Korea that apply gravity sedimentation have undergone serious operational problems because of the scum generated by algae floats (Kwak and Chung, 1998). Dissolved air flotation (DAF) is a superior process for treating the algae laden water with low turbidity (Zabel, 1985). Thus, it has been successfully applied in Korea to treat the raw water containing algae blooms that occur frequently in water bodies. Actually, the DAF process has been applied to treat the algae laden water in the two large water treatment plants such as the Wonju plant (200,000 $m^3$/day) and the southern Jeonnam plant (200,000 $m^3$/day).

On the other hand, the source water in the heavy rainy summer season usually contains high turbidity of inorganic particles attributed to the geographic slope and the characteristics of soil in Korea. The organic particles, for instance, silt, clay, sand, and grit, have a high density to settle down easily. The representative target material of those particles contained in raw water is the clay in water treatment processes. Therefore, raw water characteristics of the water treatment plant might be mainly formed by the clay particles generated

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by rainfall as well as phytoplankton such as blue-green algae. For various reasons, water treatment plants in Korea have been under two kinds of incompatible burdens.

Because of the water characteristics classifiable into these two categories, Wonju and the southern Jeonnam water treatment plant have been using a preliminary sedimentation tank to remove heavy inorganic particles, which have been considered intractable materials in the DAF process. Therefore, simultaneous removal of clay and algae particles is frequently required during the rainy season in Korea. Although the DAF unit has been successfully applied to algae-laden water treatment with low turbidity, systematic studies of the effect of high turbidity of inorganic particles caused from rainfall on DAF process are very limited. Recently, Kwak *et al.* (2005) have suggested that inorganic particles generated by rainfall highly affect the flotation efficiency.

To examine the removal efficiency of conflicting particles, the particle characteristics of clay and blue-green algae must be investigated focusing on particle separation. Thus, in this work, zeta potential and particle size distribution of clay and algae particles were measured to investigate the behavior of particles under various conditions. Zeta potential and particle size are considered to be the important parameters affecting the collision efficiency between bubble and floc in the DAF process (Han *et al.*, 2001). Zeta potential was measured under various experimental conditions including source water and operational factors like a coagulant dose. On the basis of the measurement of results on zeta potential and particle size distribution, a trajectory analysis of bubble–particle collision was simulated to develop effective operation methods and design parameters for the combination processes of sedimentation and flotation.

## Methods and materials

### Experimental materials

The chemical composition of the clay used to make the artificial raw water in this experiment is shown in Table 1. Prior to sedimentation and DAF operation, the artificial raw water containing clay and algae particles was coagulated using poly-aluminium chloride (PACl). Zeta potential (Photal Otsuka ELS-8000, Japan) was measured to examine the underlying surface charge to obtain further insight into the mechanism of removal. Before and after the treatment, the residual particle size distribution was measured using a particle counter (Laser Trac, PC2004D, USA). The turbidity and chlorophyll-a concentration were measured using the turbidity meter (HACH 2100P) and spectrophotometer (HITACHI), respectively.

### Experimental apparatus

The schematic diagram of the DAF apparatus is shown in Figure 1. A series of sedimentation and flotation experiments was conducted in a batchwise manner to measure particle

**Table 1** The raw water quality and the chemical composition of clay used in this experiment

| Water quality | | | | Chemical composition of clay | | | |
|---|---|---|---|---|---|---|---|
| Stream (Yocheon) | | Reservoir (Kyungcheon) | | Specification, wt (%) | | Specification, wt (%) | |
| PH | 6.8–7.5 | pH | 7.0–7.8 | $Al_2O_3$ | 23.14 | CaO | 2.97 |
| DO | 9.5–11.0 mg/L | DO | 9.5–11.0 mg/L | $Fe_2O_3$ | 3.92 | $K_2O$ | 1.75 |
| BOD | 1.5–2.0 mg/L | BOD | 1.2–1.8 mg/L | MgO | 1.23 | MnO | 0.03 |
| COD | 1.6–2.4 mg/L | COD | 1.5–2.2 mg/L | $Na_2O$ | 1.22 | $P_2O_5$ | 0.04 |
| SS | 1.0–5.0 mg/L | SS | 1.0–3.0 mg/L | $SiO_5$ | 62.72 | $TiO_2$ | 0.57 |
| Turbidity | 1.0–5.0 NTU | Turbidity | 1.0–3.0 NTU | Loss of ignition | 0.27 | | |

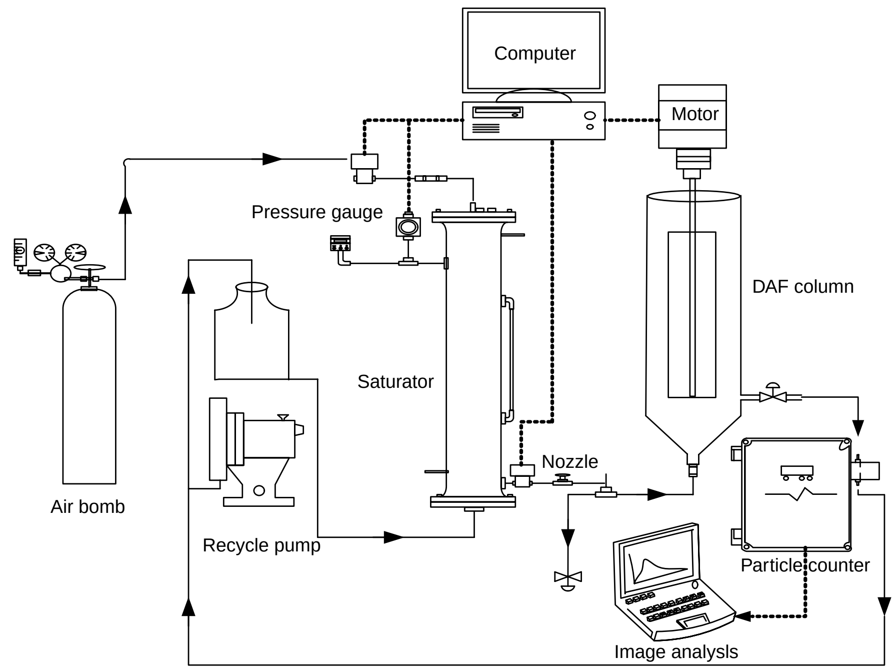


**Figure 1** The schematic diagram of DAF apparatus used in this experiment

size distribution and zeta potential under various experimental conditions as listed in Table 2.

The diameter of the flotation column made of plexiglass was 10 cm and the height was 30 cm. Algae particles in both the presence and the absence of clay were suspended initially in the column, and then bubbles were introduced in the column from the bottom side of the column. The dissolved air solution was fed through the bottom hole of the flotation column. The mean diameter of the bubbles fed into the column was about 25 μm. After all the bubbles in the cell reached the top of the column, the solution was sampled to obtain the flotation efficiency.

## Results and discussion

### Zeta potential of particles

Zeta potential is an important parameter of double layer repulsion for individual particles, and it can usually be used to interpret the trend of coagulation efficiency (Fukushi *et al.*, 1995). It has been known that colloidal particles should have zero net surface charge (isoelectric point, IEP) for agglomeration. This can result from the adsorption of

**Table 2** Operation parameters in this experiment

| Unit process | Description | Sedimentation | Flotation |
|---|---|---|---|
| Coagulation | Mixing time | 1 min | 1 min |
| | Mixing speed | 150 rpm | 150 rpm |
| Flocculation | Mixing time | 10 min | 10 min |
| | Mixing speed | 50 rpm | 50 rpm |
| Sedimentation/flotation | Contact time | | 1–2 min |
| | Separation time | 20 min | 5 min |
| Chemicals | Coagulant | PACl | PACl |
| | Dose of coagulant | 10–50 ppm | 10–50 ppm |
| | Alkalinity agent | NaOH | NaOH |
| | Dose of alkalinity | 5–20 mg/L | 5–20 mg/L |

hydrogen ions or positive-charged ions, such as ferric ions, on negative-charged surfaces. When the zeta potential of particles is approaching towards zero, coagulation efficiency is generally improved. All the zeta values measured in this experiment were the mean values of replicate observations (five to ten times).

*Coagulant dosages*. The zeta potential of two types of conflicting particles (algae and clay) was investigated in terms of solution pH (4–9) and coagulant dose (10–50 mg/L). Our experimental results showed that the variation of zeta potential was highly sensitive to the coagulation conditions. From Figures 2 and 3, it could be discriminated that the zeta potential of algae particles was higher and more fluctuant than that of clay particles as it was in the case of water characteristics.

*Removal efficiency*. In general, the maximum removal efficiency was observed around isoelectric point (i.e., 0 mV). The removal efficiency of clay and algae particles was the highest at the peak of zeta potential (Figure 3). The results imply that the variation of zeta potential is directly related to removal efficiency. Practically, the removal efficiency of algae particles fluctuated highly, which might have been caused by the larger variation of zeta potential of algae particles compared with clay particles. These findings led us to conclude that the control of zeta potential of particles such as the optimization of coagulant dosage should be carefully performed to provide effective treatment conditions for particle separation in the DAF process.

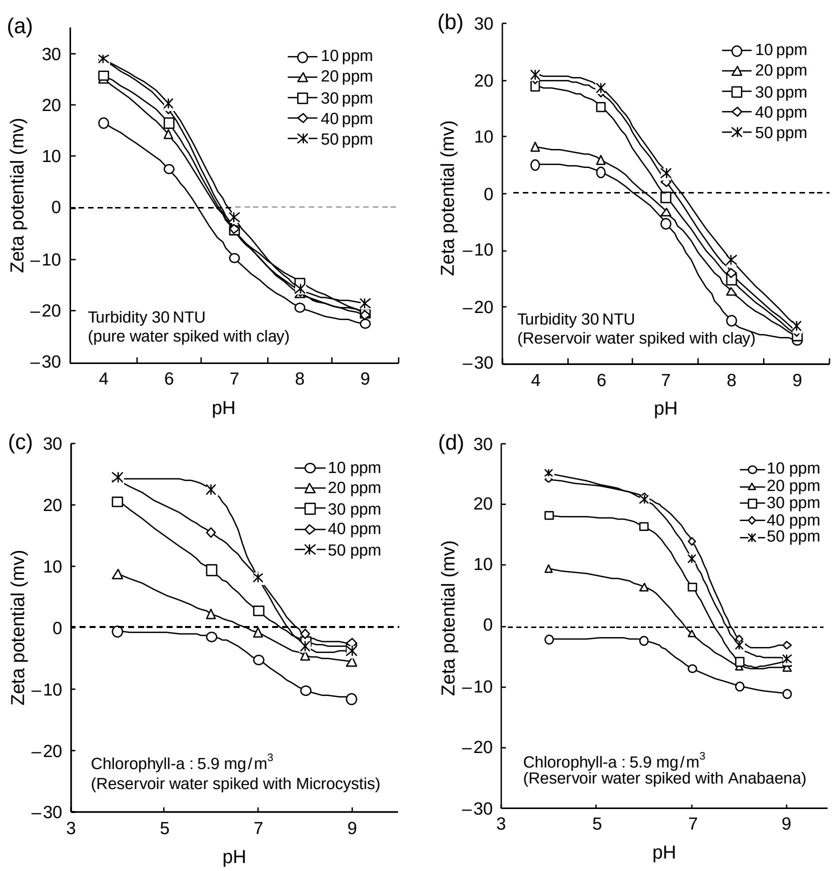


**Figure 2** Variations of zeta potential for two types of particles depending on coagulant dosages

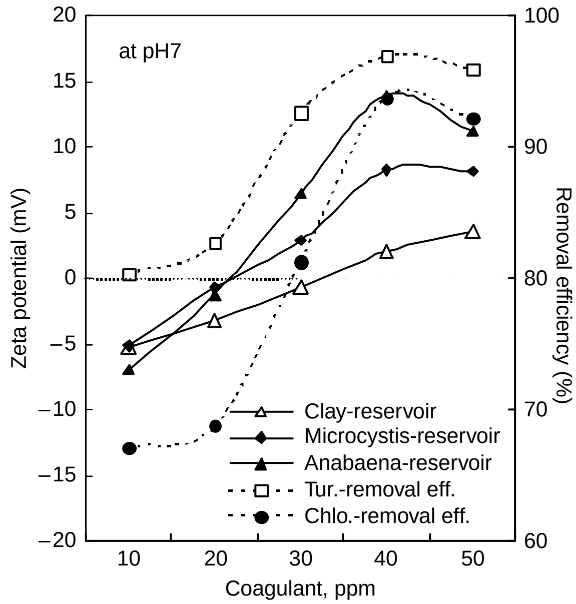


**Figure 3** Variation of removal efficiency and zeta potential depending on coagulant dosage

To verify the relationship between the zeta potential of the particles and the removal efficiency, the distribution of zeta potential values was compared with the removal efficiency of flotation for those two types of particles on the basis of coagulant dose (10–50 mg/L) derived from the measurement of turbidity and chlorophyll-a (Figure 4). The turbidity removal efficiency also revealed a tendency similar to the chlorophyll-a removal efficiency of *Microcystis* sp. and *Anabaena* sp. was increased depending on the coagulant dosages. The experimental results revealed that the removal of various particles that are contained in raw water could not be successfully achieved without employing the zeta potential of particles in the DAF process. Further works will continue to verify how much zeta potential affects the removal of algae with high turbidity based on the measurement of zeta potential and size distribution under the coexisting condition of clay and algae particles.

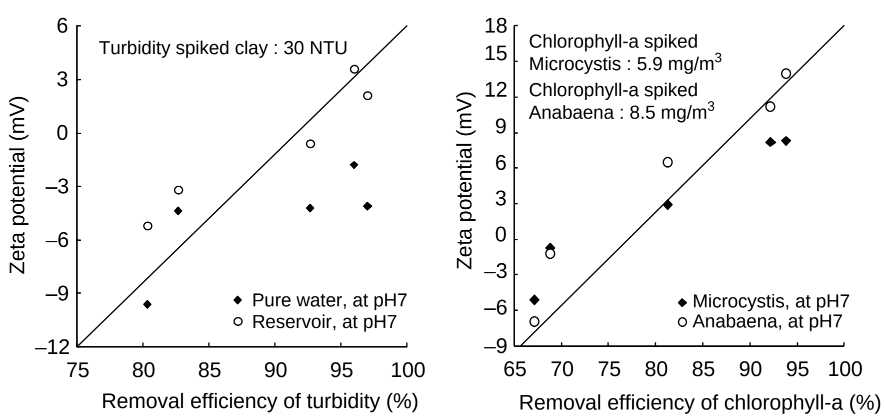


**Figure 4** Influence of coagulant dosage on the relationship between removal efficiency and zeta potential

#### Particle size distribution

It is widely known that a conventional gravity sedimentation (CGS) unit can be applied to remove clay particles generated from rainfall as a pretreatment process of DAF unit in a water treatment plant. In that case, the particle size distribution of the influent in flotation tank may change (Ceronio and Haarhoff, 2005). In this experiment, the particle size distribution was measured while a sedimentation tank was applied as an additional process to remove clay particles before the DAF process in the water treatment plant. The measurement was repeated over five times each, and the curve of the average values is shown in Figure 5.

*CGS and DAF compared*. The particle size distribution of the raw water spiked with clay and the particles remaining after sedimentation or flotation is shown in Figure 5. In this experiment, the particle size distribution was measured to compare CGS and DAF and to find the difference in removal fraction between sedimentation and flotation. The results of particle size distribution revealed that the remaining particles after sedimentation were smaller than those remaining after flotation. Therefore, when a settling tank is applied to remove inorganic particles, it is recommended that the target range of the particle size of the DAF process be concentrated on small particles.

The residual particles after sedimentation were removed mostly by flotation (Figure 6). However, some small particles still remained. Our results of the particle size distribution indicated that a control of operation condition or design parameter of small particles is required to optimize the removal efficiency in the DAF process.

*Zeta potential of small particles remaining after CGS*. The zeta potential of small particles remaining from the additional sedimentation tank was measured to explore the possibility of compensating a low separation efficiency of clay particles in the DAF process. Since the particle size distribution not removed by sedimentation was smaller than that of flotation, and since the zeta potential of residual particles was close to isoelectric or positive point, those particles were not so hard to remove. When a sedimentation tank is applied to remove clay particles as a pretreatment process of

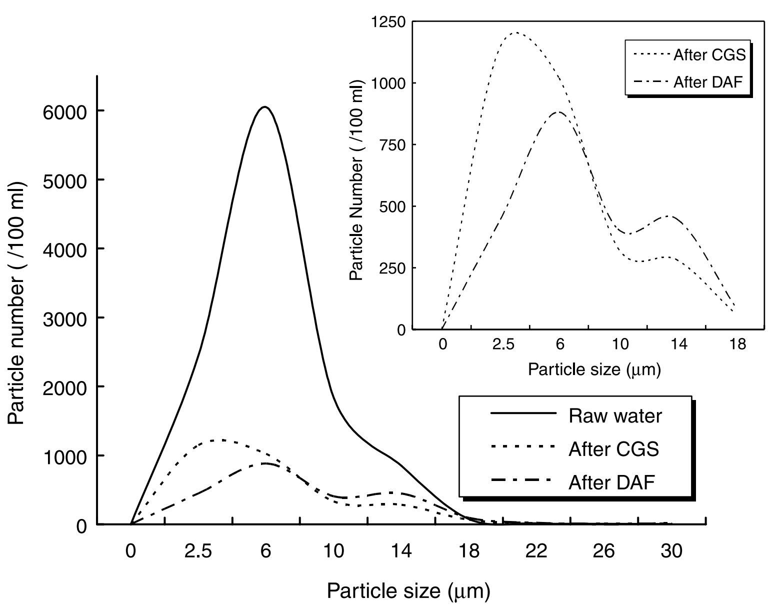




**Figure 5** Comparison of particle size distribution between sedimentation and flotation

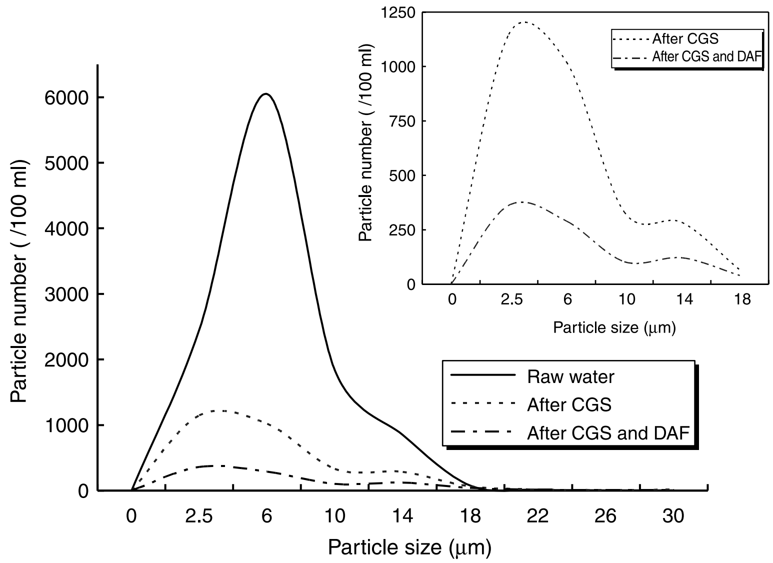


**Figure 6** Change of particle size distribution by flotation after sedimentation



flotation, the whole particle removal efficiency depends on how many small particles are removed in the course of particle separation. In particular, for separation of small particles remaining after sedimentation, the sufficient zeta potential difference between bubbles and remaining flocs is important in compensating for the decrease in the bubble–floc collision efficiency of small particles.

#### Collision and removal efficiency

On the basis of typical equations with which the inter-particle potential is calculated from DLVO theory, a trajectory analysis was performed on the collision efficiency between bubbles and particles applying the result of this study and the typical operational condition of the DAF process. Several researchers (Leppinen, 1999; Han *et al.*, 2001) developed a mathematical model to perform a trajectory analysis and to calculate collision efficiencies between the rising bubble and falling particle. The model incorporates the hydrodynamics of two particle interactions with interparticle forces. It is assumed that the bubble and particle concentrations are sufficiently small so that higher-order interactions are negligible. Parameters used in trajectory analysis are well described elsewhere (Leppinen, 1999).

*Collision efficiency by zeta potential.* The collision efficiency was simulated for the zeta potential of two types of particles to predict the removal efficiency by a trajectory analysis. Figure 7 shows the predicted values of collision efficiency that fitted well with the removal efficiency of two general algae particles. On the other hand, the removal efficiency of clay particles also showed a trend similar to collision efficiency.

*Collision efficiency of small particles.* The collision efficiency was simulated with respect to size ratio to predict the removal efficiency of the small particles by a trajectory analysis of bubble-particle. The results of the trajectory analysis showed that the collision efficiency of small particles was very low in the common range of bubble size (Figure 8). To overcome the decrease of removal efficiency by the low collision efficiency of the small particles, enlargement of the small particles by sufficient coagulation could be

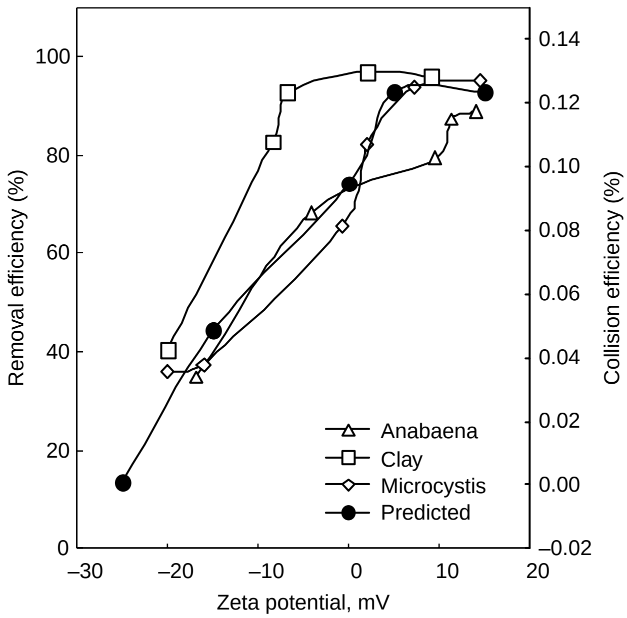


**Figure 7** Comparison of collision efficiency and removal efficiency in terms of zeta potential

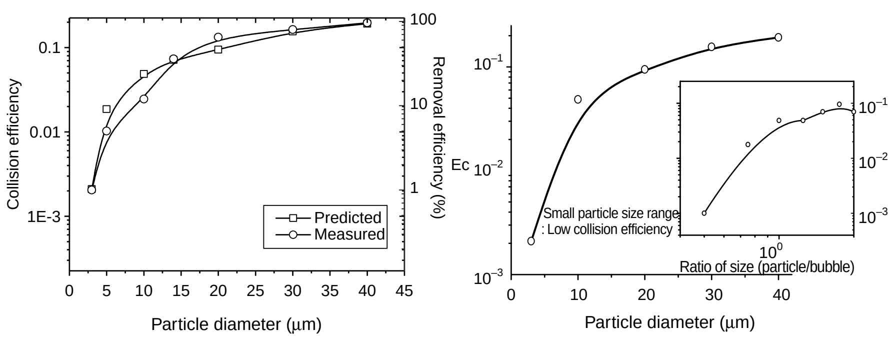


**Figure 8** Comparison of collision and removal efficiency in terms of particle diameter

considered first. However, it is known that enlargement of the small particles by coagulation has a practical limit. Subsequently, to enhance a treatment condition for effective removal of the small particles, decreasing of the bubble size or increasing of the bubble concentration could be applied. But equipment useful to freely control bubble size are not yet developed and increasing the bubble concentration also gives rise to other ineffective operation, for instance, high rate recycle ratio and high pressure of saturator. Therefore, without any additive operation or equipment, the most effective and preferential method would be an optimization of coagulation to provide sufficient zeta potential difference between bubbles and the small particles in the course of coagulation.

## Summary and conclusions

Zeta potential of two types of particles (clay and blue-green algae) was measured under various experimental conditions including several kinds of source water and coagulant dosage. In addition, particle size distributions were also measured to find a more reliable size range for effective particle separation of raw water when an additional sedimentation tank was applied to compensate for a low separation efficiency of clay particles in the DAF process.

The zeta potential of two types of particles was more sensitive to the coagulation dosage than the raw water characteristics. On the other hand, zeta potentials of blue-green algae particles fluctuated more and were more sensitive to coagulant dosage than those of clay. For that reason, the removal efficiency of algae particles fluctuated highly depending on the zeta potential of algae particles. The measurement of particle size distribution revealed that particles remaining after sedimentation were comparatively smaller than those in flotation. However, the zeta potentials of the remaining particles were close to the isoelectric point or positive charge, and it was easy to remove the particles using the DAF process. These findings led us to conclude that the control of zeta potential of particles such as the optimization of coagulant dosage should be performed with care to provide effective treatment conditions for particle separation in the DAF process.

To predict the removal efficiency of small particles by a trajectory analysis of bubble-particle, the collision efficiency was simulated with respect to size ratio. The results showed that the collision efficiency was very low. To overcome the low bubble–floc collision efficiency of small particles by optimizing of coagulation for the small particle separation remaining from sedimentation, without any additional operation or equipment, the most effective and preferential method would be an optimization of coagulation to provide sufficient zeta potential difference between bubbles and the small particles in the course of coagulation.



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